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Research Article

MISCIBILITY, THERMAL AND MECHANICAL STUDIES OF METHYLCELLULOSE/POLY (VINYL ALCOHOL) BLENDS

GS. Guru[1], P. Prasad[1], HR. Shivakumar[1]* and SK. Rai[2]

[1]Department of Chemistry, KVG College of Engineering, Sullia, D.K. Karnataka, India.

[2]Department of Polymer Science, University of Mysore, Mandya, Karnataka, India.

ABSTRACT

Miscibility characteristics of Methylcellulose (MC) and Poly (vinyl alcohol) (PVA) have been investigated by viscometry, ultrasonic velocity, density and refractmetric techniques at 30°C and 40°C. Blend films of Methylcellulose/ Poly (vinyl alcohol) were prepared by solution casting method and studied by Scanning electron microscopy (SEM) and differential scanning calorimeter (DSC) techniques. Using the viscosity data, interaction parameters of Chee's (μ) and Sun's (α) were computed to determine their miscibility. The values revealed that the components were miscible only when PVA content is 70% and below in the blend compositions of Methylcellulose/Poly (vinyl alcohol) at 30°C and 40°C. The results were then confirmed by ultrasonic velocity, density, refractive index, SEM and DSC techniques. Further, the results revealed that, the change in temperature had no effect on the miscibility of blends. To study the thermal and mechanical characteristics of blends, TGA and tensile properties were measured. Results revealed that thermal degradation temperature of the methyl cellulose increases with increase of PVA content in the blend.

Keywords: blends, viscosity, ultrasonic, density and scanning electron microscopy.

INTRODUCTION

Blending of polymers is one of the simplest means to obtain a variety of physical and chemical properties from the constituent polymers[1]. The gain in newer properties depends on the degree of compatibility or miscibility of the polymers at a molecular level. Generally, the polymer-polymer miscibility is due to some specific interactions like dipole-dipole forces, hydrogen bonding and charge transfer complexes between the polymer segments [2-5].

A literature survey reveals various techniques of studying the miscibility of polymer blends [2]. Chee [6] and Sun et al.[7] have suggested viscometric method for the study of polymer-polymer miscibility. Singh and Singh et al. [8,9] have suggested the ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Jun wuk park et al. [10] have suggested the SEM Method to determine the miscibility of polymer. Vijayalakshmi Rao et al. [11] have suggested the diferential scanning calorimetric (DSC) method to determine the miscibility of polymer. As a part of our research program, we have studied the miscibility of Methylcellulose/PVA blends in solution at different temperatures by viscosity, ultrasonic velocity, density and refractive index techniques. The solid state miscibility was studied by analysing DSC and SEM of blend films. The thermal degradation behaviors of the blends were studied by thermogravimetric analysis. The studies relating to determination of mechanical properties of the films were carried out using universal testing machine. We have selected these polymers because they have many

pharmaceutical applications[12]. Methylcellulose is a cellulose derivative that can be prepared from the reaction of alkali-cellulose with dimethyl sulfate (DMS) or methyl chloride [12,13]. It may be used as thickener in the food industry, as a matrix for controlled release of drugs in pharmaceutical industry[14]. PVA industrially produced in large quantities from the hydrolysis of poly (vinyl acetate). Because of its unique properties of solubility and biodegradability as well as biocompatibility it finds several applications and its utilization is growing steadily in recent years [15,16].

MATERIALS AND METHODS

Polymers used for the present study are Methylcellulose and Poly (vinyl alcohol). The molecular weight of methylcellulose (3000 cps at 20 ^{o}C) and PVA, 14,000 respectively. For viscometric, ultrasonic, density and refractive index measurements, dilute polymer solution of 0.5% w/v were prepared and used. Stock solution of methylcellulose and PVA and their blend composition 100/0, 10/90, 70/30, 50/50, 30/70, 10/90 and 0/100 were prepared in common solvent water. Viscosity measurements were made at 30^{o}C and 40^{o}C by using Ubbelohde suspended level viscometer (USLV). Temperatures were maintained in a thermostat bath with a thermal stability of ± 0.05 ºC. Ultrasonic velocity measurements were performed by an ultrasonic interferometer technique. During the experiment, temperatures 30^{o}C and 40ºC were maintained by circulating water from thermostat with a thermal stability of ± 0.05ºC, through the double walled jacket of the ultrasonic experimental cell. The experimental frequency was 2MHz. Density and refractive index of the blend solutions were measured at 30 and 40 ºC using specific gravity bottle and refractometer respectively. For DSC and SEM studies, thin film of Methylcellulose, PVA and their blends were prepared by solution casting method. Films were dried using IR Lamp. DSC measurements were performed in TA Q200 Differential scanning calorimeter, under nitrogen atmosphere. In DSC measurements, heating/cooling method was used. In first cycle of measurements, sample was heated to 90^{o}C and equilibrated to remove remaining water content in the sample. The sample was then cooled to -10^{o}C and reheated to 250^{o}C. The heating/cooling rate was set at 10^{o}C.

Scanning electron microscopic analysis were recorded using a JOEL (JSM 6380LA) analyzer. Thermogravimetric analysis of the blend films were performed over temperature range of 20 – 500^{o}C, using Thermogravimetric analyzer (TGA Q50 V20.2 Build 27) under nitrogen environment at a scan rate of 20 ^{o}C/min. Mechanical properties of blend films were measured under tensile strain. Five samples (10 x 150mm) for each film were tested for mechanical properties. Before testing, all the samples were conditioned for two days. Thicknesses of the samples were measured with a micrometer having a sensitivity of 1µm are found to be 0.08mm. Tensile strength at yield (TS) and percentage of elongation at break (E) were determined with an LLYODS UK model analyzer (LR 100K) according to ASTM D882 the test was run at 100mm/min and at room temperature.

RESULTS AND DISCUSSION

From Viscometric measurements, reduced viscosities of homo-polymers and their blend compositions (100/0, 90/10, 70/30, 50/50, 30/70, 10/90, 0/100) were measured at 30^{o}C and 40^{o}C. Reduced viscosities of the pure polymers and their blend compositions are plotted against concentrations are shown in Figure 1 and 2 respectively. From these Figures 1 and 2, it is clear that the Huggin's plots are composed of two regions with varying slopes for Methylcellulose/PVA blends. In the present work Figures 1 and 2 indicates considerable higher slopes for 90/10, 70/30, 50/50 & 30/70 blend at 30^{o}C and 40^{o}C respectively. This is may be attributed to the mutual attraction of macromolecules in solution which leads to increase of hydrodynamic volume. Thus, methylcellulose/PVA blend is found to be miscible, when PVA content is 70% and below in blend compositions at 30^{o}C and 40^{o}C. Above this critical concentration, a sharp decrease in the slope is observed in the Huggin's plot due to phase separation.

In order to quantify the miscibility of polymer blends, Chee [6] suggested the general expression for interaction parameter when the polymers are mixed in weight fractions w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2 w_1 w_2} \qquad (1)$$

where $\bar{b} = w_1 b_{11} + w_2 b_{22}$ where b_{11} and b_{22} are the slopes of the viscosity curves for the components and b is related to Huggins coefficient K_H as,

$$b = K_H[\eta]^2 \quad (2)$$

For ternary system, it is also given by

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12} \quad (3)$$

where b_{12} is slope for the blend solution.
However, Chee's theory fails to account for the experimental data when intrinsic viscosities of pure components are far apart. In such cases he defined a more efficient parameter to predict compatibility,

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \quad (4)$$

where $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities of pure component solutions. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.
Later Sun et al.[7] have suggested a most satisfactory new equation for the determination of polymer miscibility as

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2(K_1K_2)^{1/2}[\eta]_1[\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \quad (5)$$

where K_1, K_2 and K_m are the Huggins constants for individual components 1, 2 and blend respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.
The interaction parameters Chee's (μ) and Sun's (α) of the blend compositions at 30°C and 40°C are presented in the Table 1. Computed values of interaction parameters μ and α were found to be positive at 90/10, 70/30 and 50/50 compositions at 30 and 40 °C. The μ value is found to be negative for 30/70 composition at 30 and 40 °C, but α value was found to be positive. Since the secondary interactions are taken into account in computing α value, the equation (5) is more accurate than equation (4). Similar observations were made by Raviprakash et al. [17] and Varadarajulu et al.
To confirm this further, we have measured ultrasonic velocity (υ) density (ρ) and refractive index (n) of the blends under consideration at different compositions at 30°C and 40°C. The variations in ultrasonic velocity, density and refractive index with the blend compositions are shown in Figures 3, 4 and 5 respectively. The Adiabatic compressibility B_{ad} [19] of different blend composition evaluated by using following equation (6):

$$\beta_{ad} = 1/(\upsilon^2 \rho) \quad (6)$$

where (υ) is the ultrasonic velocity and (ρ) is the density. The graphs show both linear and non linear regions. It has been already established that the variation is linear for miscible blend and non linear for immiscible blend [6,8]. In the present case, the variation was found to be linear when the PVA content is 70% and below in Methylcellulose/PVA blend compositions at 30°C and 40°C. This observation is in confirmation with μ and α value. So the present study indicates the existence of miscibility when PVA content is less than 80% in the blends. Intermolecular hydrogen bonding between hydroxyl groups of the methylcellulose and PVA may be responsible for the miscibility in the above compositions.

Morphology Study of Methylcellulose/PVA blends

Scanning electron microscopy (SEM) is a powerful technique to determine miscibility of polymer blends[10,20]. The uniformity of the dispersion of the solution cast films of 100/0, 90/10, 70/30, 50/50, 30/70 and 0/100 MC/PVA blend compositions was examined through SEM and the corresponding micrographs are as shown in Figures 7 (a, b, c, d, e and f). At a low content of PVA in the blend, PVA was dispersed completely and showed single phase and when PVA content was increased, blend films showed rough surface which can be observed in SEM. This may be due to high viscosity of PVA. The solid state study of blend also confirmed the semi-compatible nature of the blend.

Glass transition temperature (Tg) measurements:

The glass transition temperature (Tg) of indivdual polymers and their blends are recorded from the DSC thermograms, blends exhibited a single Tg, for the blend compositions of 91/10, 70/30, 50/50 and 30/70 respectively. The glass transition temperature was taken as the mid point of the change of slope in DSC curves [21]. The Tg of miscible blends can be predicted by using the Fox equation [22] (7) or Woods equation [23] (8)

$$1/Tg = X_1/Tg_1 + X_2/Tg_2 \quad \text{--------- (7)}$$
$$Tg = W_1Tg_1 + W_2Tg_2 \quad \text{--------- (8)}$$

Where X_1, X_2, Tg_1 and Tg_2 are the weight fractions and glass transition temperature of the corresponding to polymer 1 and polymer 2 respectively.

The experimental Tg value for 91/10, 70/30, 50/50 and 30/70 Methylcellulose/PVA blends compared with theoretical Tg vales are summarized in Table 2. The experimental Tg value for 91/10, 70/30, 50/50 and 30/70 Methylcellulose/PVA blends found to be slightly higher than that of theoretical calculated Tg values implying an intermolecular interaction between the polymers.[24]

Thermogravimetric Analysis (TGA)

Thermal stability of Methylcellulose, poly (vinyl alcohol) and their blend films were assessed. Typical TGA and their derivative thermogram for Methylcellulose, poly (vinyl alcohol) and their blend films (100/0, 70/30, 50/50, 30/70, 10/90, 0/100) are shown in Figure 9. Methylcellulose shows single stage degradation, the temperature at which it a start to decompose is exceptionally high 250^{o}C and ends at 375^{o}C. Poly (vinyl alcohol) shows multi-stage degradation, at 95^{o}C it involves dehydration and successive degradation appears between 190^{o}C to 280^{o}C and 330 to 400^{o}C. The 70/30 blend composition of Methylcellulose/poly (vinyl alcohol) shows only a single stage degradation that occurs between 220^{o}C and 390^{o}C. Fragmentation of blend occurs during the degradation yielding volatile fragments. The degradation of 50/50 blend is found to follow similar pattern and shows only single stage degradation occurs between 210^{o}C and 390^{o}C. The degradation of 30/70 and 10/90 blend composition is found to be two stage degradation , in 30/70 blend first stage begins at 190^{o}C and ends at 275^{o}C with a peak temperature at 268^{o}C. This corresponds to a weight loss at 268^{o}C is 0.5081% /^{o}C .The second stage degradation begins at 320^{o}C and ends at 390^{o}C with a peak temperature at 358^{o}C. In 10/90 blend first stage begins at 180^{o}C and ends at 265^{o}C with a peak temperature at 266^{o}C. The second stage degradation begins at 290^{o}C and ends at 385^{o}C with a peak temperature at 362^{o}C. This clearly indicates from thermogram of Methylcellulose/PVA that, initial degradation temperature of methylcellulose decreases with increase of PVA, but final degradation temperature of the blends increases, that have been calculated and given in the Table 3 respectively.

Mechanical properties

Mechanical properties of blend films were measured under tensile strain, the tensile strength which is a measure of the resistance. The tensile strength at yield and elongation at break of methylcellulose, PVA and their blend films (100/0, 10/90, 70/30, 50/50, 30/70, 10/90 and 0/100) were measured and given in Table 4. The tensile strength at yield and elongation at break were found to be 36.16 Mpa, 21.67 % and 20.26 Mpa, 53.46 % for pure Methylcellulose and PVA. The observed values of tensile strength at yield and elongation at break of blend films are showed increase in its mechanical properties as the PVA content is increase in blend compositions, except 30/70 composition of Methylcellulose/PVA blend, may be due to lack of interaction between components of polymers. At 90/10 Methylcellulose/PVA blend composition blend film shows large increase in tensile strength at yield and elongation values due to strong hydrogen bonding between the components of the polymers.

Table 1: Interaction parameters μ and α of Methylcellulose/PVA blends at 30°C and 40°C

Methylcellulose/PVA blend compositions	At 30ºC		At 40ºC	
	μ- values	α-values	μ- values	α-values
90/10	+3.6208	+0.3977	+3.1882	+0.3130
70/30	+1.9727	+0.8881	+1.4607	+0.1616
50/50	+0.1728	+0.7223	+0.1144	+0.7355
30/70	- 0.0983	+0.4426	- 1.9550	+0.3754
10/90	- 4.1270	- 0.1994	- 3.5020	- 0.3764

Table 2: Experimental and Theoretical Tg values of Methylcellulose and PVA and their blends

Methylcellulose/PVA Compositions	Experimental Tg values (ºC)	Theoretical Tg values (ºC)	
		Fox equation	Wood's equation
100/0	37.00	-	-
90/10	39.98	38.50	39.35
70/30	44.64	41.88	44.05
50/50	49.13	46.69	48.75
30/70	54.10	50.83	53.45
0/100	60.50	-	-

Table 3: Data obtained from TGA scans for Methylcellulose/PVA blend films

Methylcellulose/PVA blend compositions	Temperature at which 20% weight loss	Temperature at which 80% weight loss
100/0	321	365
70/30	318	380
50/50	290	420
30/70	270	385
10/90	263	335
0/100	260	430

Table 4: Mechanical properties of Methylcellulose/PVA blend films

Methylcellulose/PVA blend compositions	Tensile strength at yield (MPa)	Elongation at break (%)
100/0	36.16	21.67
90/10	52.74	42.65
70/30	35.50	25.30
50/50	22.05	21.96
30/70	18.29	17.22
10/90	16.44	14.23
0/100	20.26	53.46

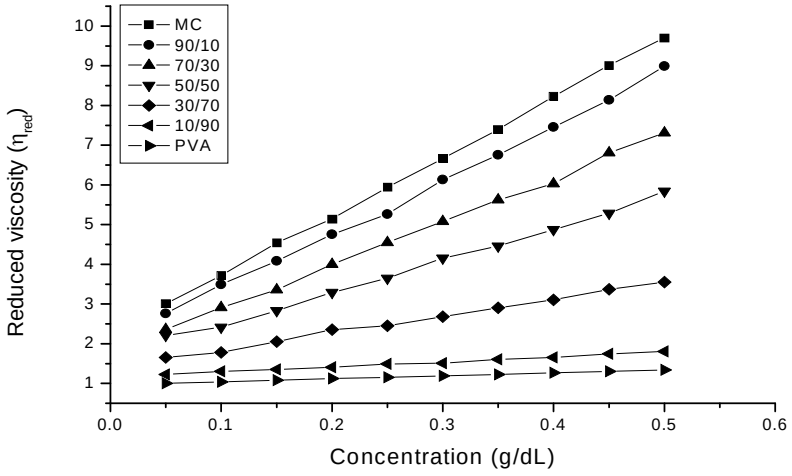

Fig. 1: Huggin's plot for 0.5 % w/v Methylcellulose/PVA blend in solution at 30°C

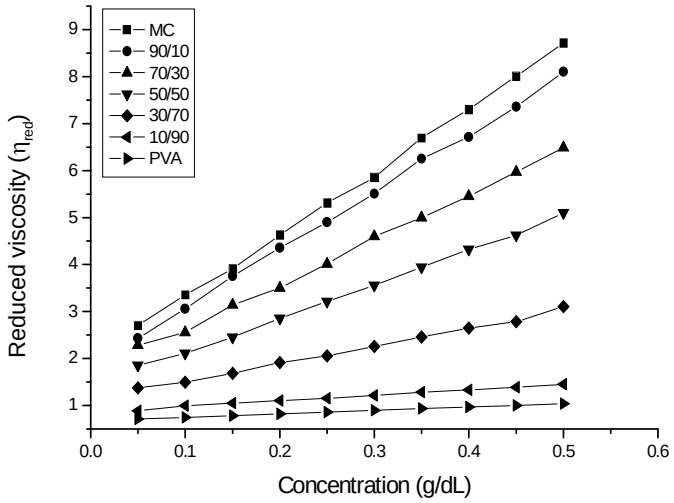

Fig. 2: Huggin's plot for 0.5 % w/v Methylcellulose/PVA blend in solution at 40°C

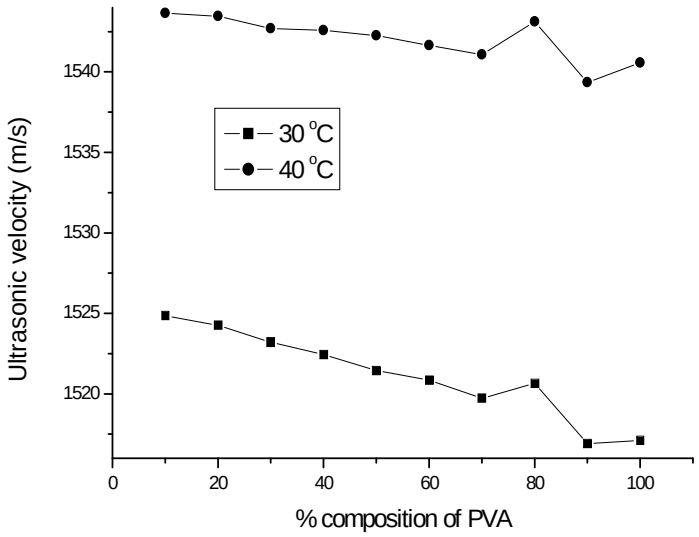

Fig. 3: Effect of temperature on the variation of Ultrasonic velocity with the composition of 0.5 % w/v of Methylcellulose/PVA blend at 30 and 40°C

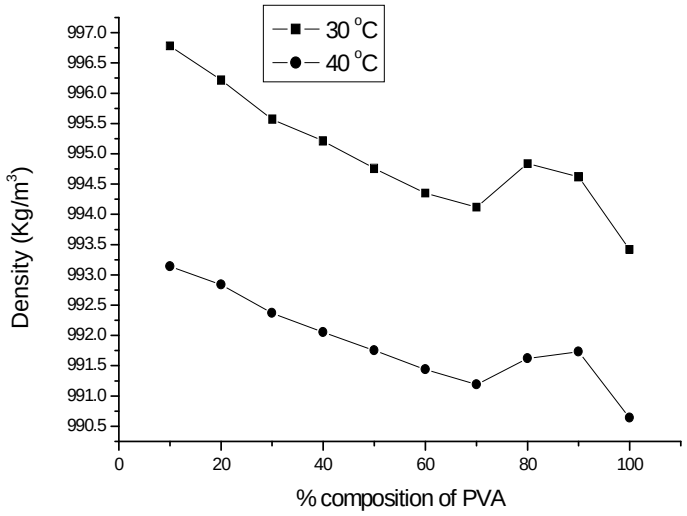

Fig. 4: Effect of temperature on the variation of density with the composition of 0.5 % w/v of Methylcellulose/PVA blend at 30 and 40°C

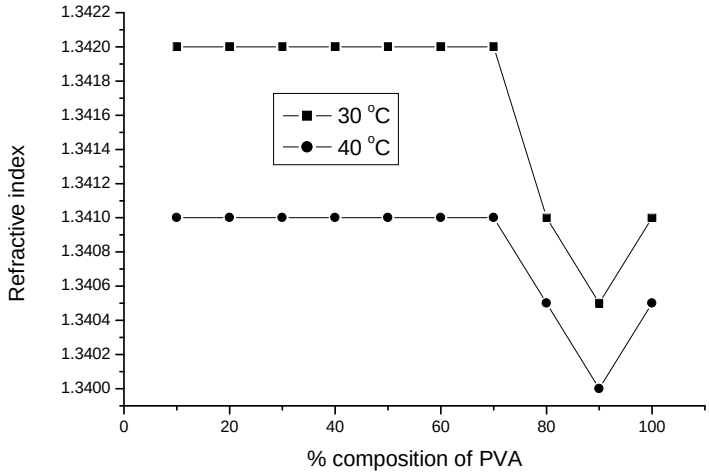

Fig. 5: Variation of Refractive index with the composition of 0.5% w/v of Methylcellulose/PVA blend at 30 and 40°C

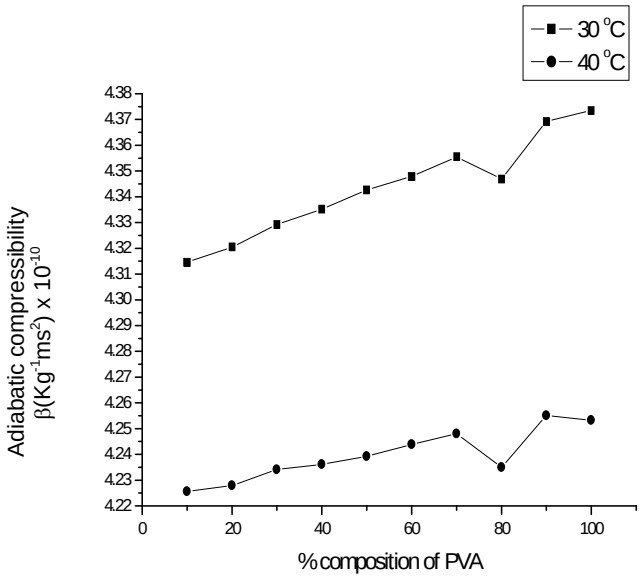

Fig. 6: Effect of temperature on the variation of Adiabatic Compressibility with the composition of 0.5 % w/v of Methylcellulose/PVA blend at 30 and 40°C

Scanning electron microscopy (SEM) is a powerful technique to determine miscibility of polymer blends. The uniformity of the dispersion of the solution cast films of 100/0, 90/10, 70/30, 50/50, 30/70 and 0/100 MC/PVA blend compositions was examined through SEM and the corresponding micrographs are as shown in Figures 5.8 (a, b, c, d, e and f). At a low content of PVA in the blend, PVA was dispersed completely and showed single phase and when PVA content was increased, blend films showed rough surface which can be observed in SEM. This may be due to high viscosity of PVA. The solid state study of blend also confirmed the semi-compatible nature of the blend.

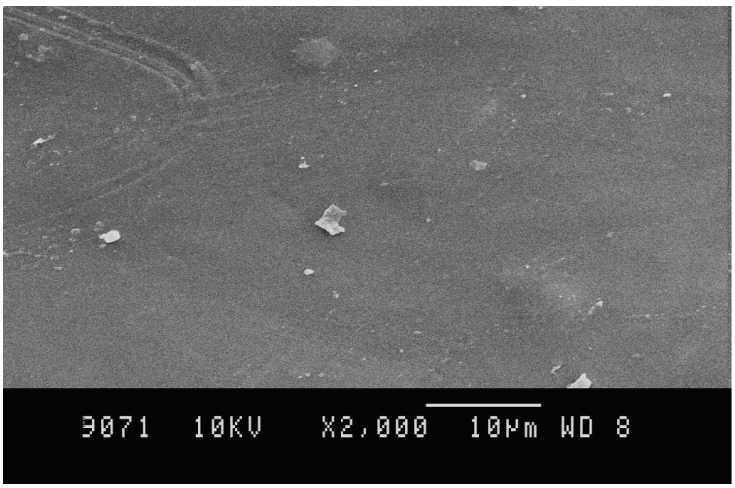

Fig. 7 a) Pure Methyl cellulose (MC)

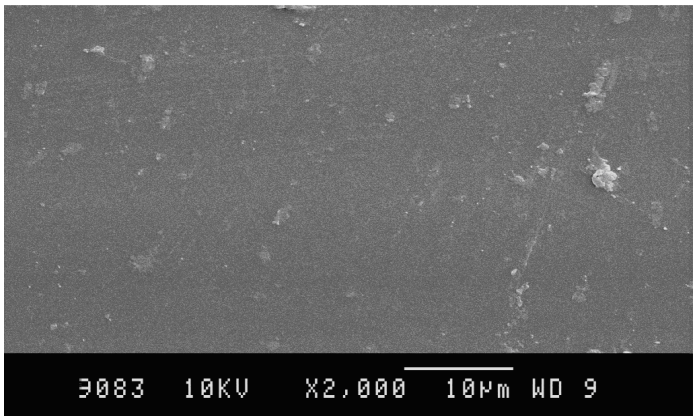

Fig. 7 b) Pure PVA

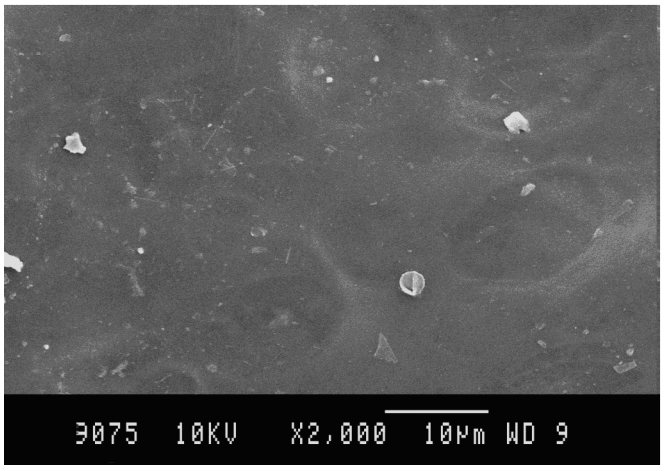

Fig. 7 c) 90/10 MC/PVA blend

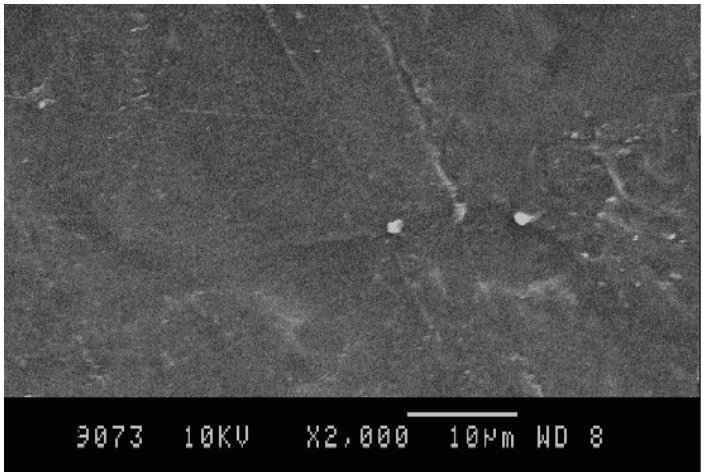

Fig. 7 d) 70/30 MC/PVA blend

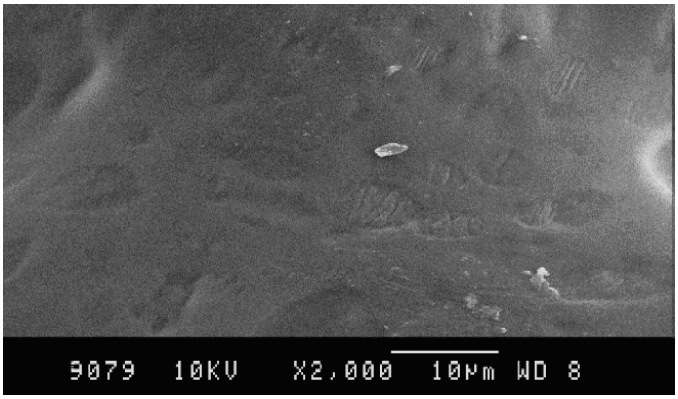

Fig 7 e) 50/50 MC/PVA blend

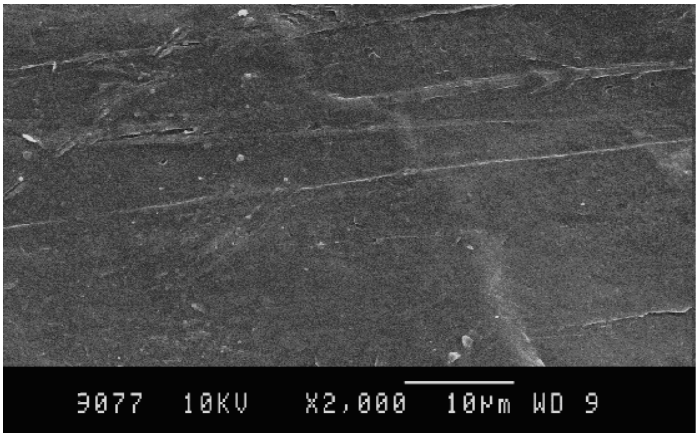

Fig. 7 f) 30/70 MC/PVA blend

Fig. 7: Scanning electron micrographs for a) Pure MC, b) Pure PVA, c) 90/10 MC/PVA blend, d) 70/30 MC/PVA blend, e) 50/50 MC/PVA blend and f) 30/70 MC/PVA blend

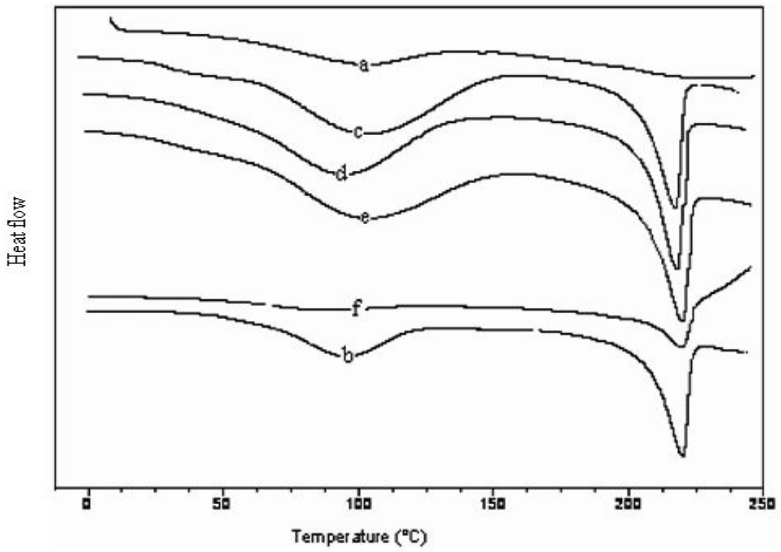

Fig. 8: DSC thermograms of (a) Pure Methylcellulose (b) Pure PVA (c) 90/10 MC/PVA blend (d) 70/30 MC/PVA blend, (e) 50/50 MC/PVA blend and (f) 30/70 MC/PVA blend.

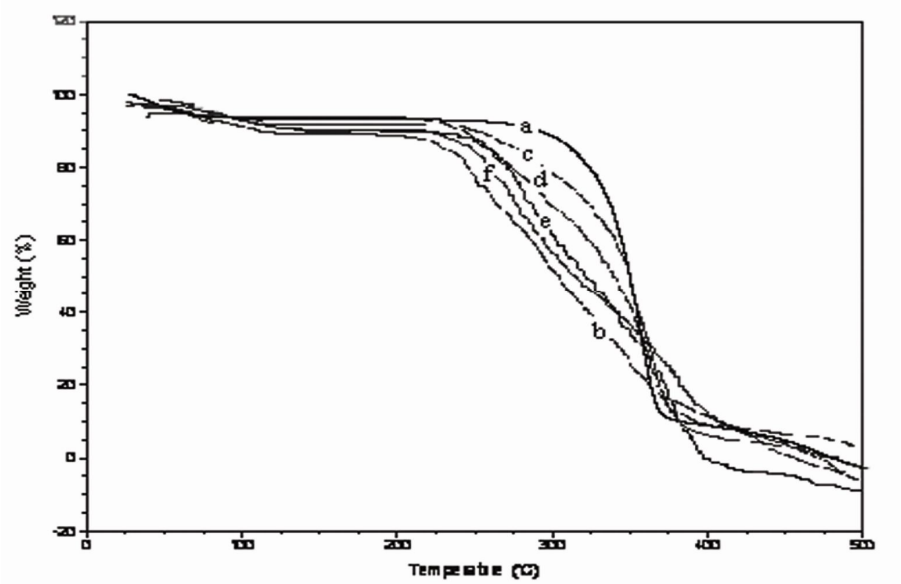

Fig. 9: TGA thermograms of (a) Pure Methylcellulose (MC), (b) Pure PVA, (c) 70/30 MC/PVA blend, (d) 50/50 MC/PVA blend, (e) 30/70 MC/PVA blend and (f) 10/90 Methylcellulose/PVA Blend

CONCLUSION

Based on viscosity, ultrasonic velocity, and density measurements, it is concluded that blend of Methylcellulose/PVA was found to semi-compatible at 30°C and 40°C. It was observed that change in temperature of 10°C did not have any effect on the miscibility of Methylcellulose/PVA blend compositions. The semi-compatible nature of the blend was also confirmed by DSC and SEM studies. The thermal and mechanical properties improved in the blend compositions were observed.

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